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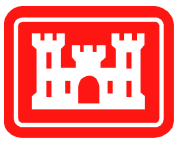

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Estimating the Half-Lives of Key Components of the Chemical Vapor Signature of Land Mines

Paul H. Miyares and Thomas F. Jenkins

September 2000

Abstract: The qualitative composition of the chemical signature of TNT-filled land mines is predominantly the isomers of dinitrotoluene (DNT), dinitrobenzene (DNB), and trinitrotoluene (TNT). These chemicals are known to undergo transformation in the soil under aerobic conditions, creating corresponding chemicals in which one of the nitro groups has been converted to an amino function. For these signatures to be available at the ground surface for detecting buried mines, the stability of these chemicals in the soil must exceed their rate of transport through the soil to the surface. This research investigates the rate of transformation of the major components of the signature of TNT-filled land mines in soil. A series of 5.0-g replicate portions of soil from a research minefield at Fort Leonard Wood, Missouri, was fortified with 2,4,6-trinitrotoluene, 2,4- and 2,6-dinitrotoluene, and 1,3-dinitrobenzene at about 0.5 mg/kg. Replicates were held at one of three temperatures (22 ± 2, 4 ± 2, or –4 ± 2°C) in the dark for periods ranging from 4 hours to 30 days and were then extracted with acetonitrile. The extracts were analyzed by reversed-phase HPLC to estimate the concentrations of the parent compounds and any detectable transformation products remaining. Concentrations of these compounds were plotted versus time and the rate of transformation for each compound estimated. While it doesn't appear that the process is kinetically first order, the half-life at 22°C was estimated to be about 1.3 days for 2,4,6-TNT, 9.9 days for 1,3-DNB, 18 days for 2,6-DNT, and 26 days for 2,4-DNT. At lower temperatures the half-lives were considerably longer, as expected.

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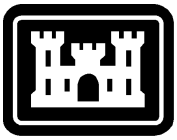
Technical Report
ERDC/CRREL TR-00-17



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Paul H. Miyares and Thomas F. Jenkins

September 2000

Prepared for
DEFENSE ADVANCED RESEARCH PROJECTS AGENCY

PREFACE

This report was prepared by Dr. Paul H. Miyares, Research Chemist, Geochemical Sciences Division, and Dr. Thomas F. Jenkins, Research Chemist, Geological Sciences Division, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire.

This work was sponsored by the Defense Advanced Research Projects Agency (DARPA), Regina Dugan, Program Manager; Vivian George was the Project Monitor. Daniel Leggett, CRREL, and Thomas Ranney, Science and Technology Corporation, provided technical review.

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PAUL H. MIYARES AND THOMAS F. JENKINS

INTRODUCTION

Detection and elimination of buried land mines remains an important and intractable problem in many countries throughout the world. The use of plastic cases on mines has reduced their detectability using magnetometry, and geophysical techniques, such as ground penetrating radar, suffer high levels of false positives. An approach that is currently under investigation is chemical detection of vapors that evolve from explosives and are transported to the air or surface soil in the immediate vicinity of buried land mines. The success of canines in locating buried mines has demonstrated that there are detectable scents (chemical signatures) at the surface in the vicinity of these mines. Research is currently underway in our laboratory and elsewhere to determine the qualitative and quantitative nature of the chemical signatures originating from the explosives within the land mines that may be detectable at the surface above buried mines. One of the critical elements in this investigation is the stability of the key components of the vapor once it enters the soil.

The ultimate goal of our research is predicting the composition and concentrations of land mine signatures at the surface above buried mines. A further goal is to predict these under various environmental conditions. For example, the chemical composition of the explosive charge in several types of foreign land mines was determined (Leggett et al. 1977) and laboratory experiments have estimated the equilibrium headspace concentrations of explosives signatures associated with a number of military-grade TNTs (Jenkins et al., in press). Experiments with a number of intact mines and mine surrogates have been conducted to estimate the flux of these compounds through the mine casing at temperatures ranging from –4 to 32°C (Leggett et al., in prep.). An initial study investigated the rate of transport of these signatures through the soil to the surface and provided some initial estimates for the surface-soil-to-air partition coefficients for signature chemicals at the soil/atmosphere interface (Jenkins et al., in press).

In the study presented here, we will investigate the degradation rates of key components of the chemical vapor signatures of explosive charges in land mines resulting from the mines being buried. We will estimate the half-lives for these chemical components in soil from a research minefield at Fort Leonard Wood, Missouri, at several different temperatures, and compare the stability observed with that found for these compounds in several different soils.

Background

The pathway for reductive transformation of nitroaromatics was first presented by McCormick and co-workers (McCormick et al. 1976). For 2,4,6-TNT, one of the three nitro groups on the aromatic ring is reduced stepwise through nitroso and hydroxylamine groups, resulting in the formation of two isomeric transformation products, 2-amino-4,6-dinitrotoluene (2ADNT) and 4-amino-2,6-dinitrotoluene (4ADNT). These two compounds are relatively stable under aerobic conditions, and have been routinely observed in TNT-contaminated surface soils (Walsh et al. 1993).

The question of the stability of nitroaromatic and nitramines in soil was first addressed by Maskarinec et al. (1991) during a study conducted to determine the pre-extraction holding times for soil samples collected at explosives-contaminated sites. In his studies, Maskarinec rewetted the soil to reestablish microbiological activity, then spiked each sample with the explosives of interest dissolved in acetonitrile (AcN). A total of 2 mL of AcN was added to each 2-g sample. From his results, Maskarinec recommended a

holding time of 6 weeks at 4°C for 1,3,5,7-octahydro-1,3,5,7-tetranitrotetrazocine (HMX), 1,3,5-hexahydro-1,3,5-trinitrotriazine (RDX), and 2,4-dinitrotoluene (2,4-DNT), and several weeks at –20°C for 2,4,6-trinitrotoluene (TNT). Although the study was carefully conducted and extensive data were collected, the work may have been flawed by the use of the AcN. The effect of the AcN on the soil biota is unknown but, more importantly, soil being stored for analysis does not contain any AcN. Thus, the samples used do not mimic real sample. In fact, AcN is the solvent of choice for the extraction of nitroaromatics and nitramines from soil (Jenkins and Grant 1987).

In 1993, a similar study was conducted in our laboratory to determine the pre-extraction holding times for select nitroaromatics and nitramines in soil (Grant et al. 1993, 1995). In this study, replicate 5-g samples of three different soils, Fort Edwards clay, Charlton sandy loam, and Windsor silt, were prepared first by rewetting, and then spiking with an aqueous solution of TNT, 2,4-DNT, RDX, HMX, and 1,3,5-trinitrobenzene (TNB). Three storage conditions were examined, room temperature (22 ± 2°C), refrigerator storage (2 ± 2°C), and freezer storage (–15 ± 2°C). Triplicate samples from each storage temperature were extracted after 0, 3, 7, 14, 28, and 56 days and the concentration of the analytes determined. The results indicated that both TNB and TNT degraded very rapidly at room temperature, so rapidly that some losses were observed even in the day 0 samples, which were extracted only 2 hours after spiking. Grant et al. (1993) go on to report significant losses of TNT and TNB at refrigerator temperatures at 7 days for all three soils and, at freezer temperatures, no losses in the Charlton and Windsor soil, but slight losses in the Fort Edwards soil at 56 days. The loss of TNT and TNB was coincident with the formation of the corresponding monoamino transformation products predicted, based on the work of McCormick et al. (1976).

In contrast, Grant et al. (1993, 1995) found that 2,4-DNT was much more stable than TNT or TNB. At room temperature, 68% of the 2,4-DNT was still present after 3 days, compared to less than 10% for both TNT and TNB. As the temperature decreased, the 2,4-DNT showed even greater stability. HMX and RDX were found to be even more stable than 2,4-DNT. For these two nitramines, no significant losses of analytes were detected at any temperature or in any of the soils for the full 56 days. Overall, these results demonstrated significant variability in the stability of the major components of explosives between various soils and at different temperatures.

In a study investigating the use of stable isotope measurements as a means of monitoring the natural attenuation of TNT, Miyares et al. (1999) found that the stability of TNT in soil varies with soil type and location. Results in the present study showed that TNT degraded much faster in a Charlton sandy loam collected in New Hampshire than in a deep aquifer sand collected in Louisiana.

Dubois and Baytos (1991) also investigated the stability of TNT in soil. In their study, however, they buried a solid chunk of TNT and studied the reduction in mass over 20 years. They concluded that the TNT exhibited a half-life of about a year. It is unlikely, though, that the mechanisms controlling the rate of TNT loss in that study are similar to those that control the rate of transformation of TNT when it is present at the parts-per-billion level in soil.

Objective

The objective of this study is to estimate the stability (half-lives) of the major land mine signature components in soil from a research minefield at Fort Leonard Wood, Missouri, at various environmental temperatures. These results will be used to help us understand the rate of accumulation of explosives signatures in soils adjacent to buried land mines at the research minefield. In addition, the stability exhibited in this soil will be compared with that found for several other soils.

EXPERIMENTAL METHODS AND MATERIALS

Chemicals

All standards and test solutions were prepared from Standards Analytical Reference Materials (SARM) obtained from the U.S. Army Environmental Center (AEC), Aberdeen Proving Ground, Maryland. Aqueous standards and test solutions were prepared in reagent grade water obtained from a Milli-Q Type 1 Reagent Grade Water System (Millipore Corp.). The isopropanol (IPA) used to prepare the HPLC eluent and the acetonitrile (AcN) used for soil extractions were HPLC grade from Burdick and Jackson. RP-HPLC eluent was prepared by combining water and IPA at a ratio of 85/15 (v/v) and vacuum filtering through a nylon membrane (0.2 mm) to degas and remove particulate matter.

Spiking solutions

Aqueous solutions of the key components of TNT vapor (Jenkins et al., in press), TNT, 1,3-dinitrobenzene (DNB), 2,4-DNT, 2,6-dinitrotoluene (2,6-DNT), and the internal standard, RDX, were prepared from SARMs. A small mass of each compound was placed in a 4-L amber glass bottle to which reagent grade water was added. The contents were stirred at room temperature for a week. The solutions were then fil-

Table 1. Concentration of aqueous stock solutions and preparation volumes for the aqueous analyte spiking solution.

Key components	*Conc. of aqu. stock (mg/L)*	*Volume of aqu. stock (mL)*	*Conc. in aqu. spiking solution (mg/L)*	*Conc. in soil (mg/kg)*
1,3-DNB	5.25	440	2.31	0.462
2,4,6-TNT	31.5	90	2.84	0.568
2,4-DNT	46.1	55	2.54	0.508
2,6-DNT	14.4	185	2.66	0.532
RDX	26.7	30	0.80	0.160

tered through 0.45-mm nylon membranes into clean, amber glass jugs. No solvents, other than water, were used in the preparation of these solutions. The concentration of each solution was determined by RP-HPLC.

A combined-analyte spiking solution of the key components was prepared by combining appropriate volumes of each of the individual aqueous solutions (Table 1) and diluting to 1 L in a volumetric flask. This solution included 1,3-DNB, 2,4,6-TNT, 2,4-DNT, and 2,6-DNT. RDX was also included, because previous research indicated that it was quite stable in soil and could serve as an internal standard to account for any minor differences in spiking volume from replicate to replicate. This solution was filtered through a 0.45-mm nylon filter, then transferred to a brown glass jug and stored in a refrigerator at 4°C. The aqueous solution was analyzed by HPLC. The determined concentrations are presented in Table 1.

Soil

The soil used for this study was obtained from the research minefield at Fort Leonard Wood. The soil was air-dried, ground with a mortar and pestle, and sieved through a no. 40 (425-mm) sieve. Replicate 5.0 ± 0.1-g subsamples were weighed into individual 20-mL glass scintillation vials.

Soil wetting and analyte spiking

Prior to the start of the experiment, we rewetted the previously air-dried test soil by adding 1.00-mL aliquots of water to each replicate. The samples were then allowed to stand at room temperature in the dark for 3 days to allow microbiological activity to be reestablished (Maskarinec et al. 1991).

The soil samples were fortified by carefully adding 1.00 mL of solution to each individual vial; 90 individual vials were spiked. To three of the replicates, 1.0 mL of reagent grade water was added as a blank, and, to the remaining 87 replicates, 1.0 mL of the combined analyte aqueous spiking solution was added. The target concentration of the analytes in the soil was approximately 0.5 mg/kg for the nitroaromatics and 0.14 mg/kg for RDX.

After spiking, samples 1 to 33 were placed in a low-temperature incubator at –4 ± 2°C, samples 34 to 63 were placed in a refrigerator at 4 ± 2°C, and samples 64 to 84 were placed in a cabinet at room temperature (22 ± 2°C) in the dark. Samples 85, 86, and 87 were the blanks (deionized water spiked) and samples 88, 89, and 90 were the time 0 samples. The time 0 samples were spiked with the aqueous solution of explosives, followed immediately by 10 mL of AcN. This was done to minimize the opportunity for analyte loss and allow for the accurate determination of the initial concentration of analytes in the samples.

Four hours from the time of spiking, triplicate sample vials from each storage temperature were selected at random. The samples from the lower temperatures were briefly allowed to warm to room temperature. A 10-mL aliquot of AcN was added to each of the nine samples. These samples, along with the three time 0 samples, were extracted overnight using ultrasonication. The extracts were then analyzed by HPLC.

The remaining samples were treated in an identical manner after additional storage at one of the three temperatures. Subsequently, triplicate samples from each storage temperature were extracted and analyzed on days 1, 3, 7, 13, and 20. Because of the rapid rate of analyte transformation at room temperature, samples from this storage temperature were also run on day 9. For samples stored at 4 and –4°C, triplicates were also run on day 30.

In addition to determining the concentrations of the key components, we also determined the concentrations of the monoamino reduction products of each nitroaromatic. These included 3-nitroaniline (3-NA), 6-amino-2-nitrotoluene (6-Am-NT), 2-amino-4-nitrotoluene (2-Am-NT), 4-amino-2-nitrotoluene (4-

Am-NT), 2-amino-4,6-dinitrotoluene (2-Am-DNT), and 4-amino-2,6-dinitrotoluene (4-Am-DNT). The spiked samples were immediately placed into the appropriate storage temperatures in the dark.

Storage parameters and hold times

As mentioned, the soils were stored in the dark at three temperatures—room temperature (22 ± 2°C), refrigerator temperature (4 ± 2°C), and freezer temperature (–4 ± 2°C). Triplicates stored under all three conditions were extracted at time 0, after 4 hours, 1 day, 3 days, 7 days, 13 days, and 20 days, and the analyte concentration determined. An additional sampling and analysis was conducted at 9 days for samples stored at room temperature and at 30 days for samples stored at 4 and –4°C. Because of the expected variability among replicates, triplicate vials were analyzed for each storage temperature for each storage time.

Soil extraction

For soil extraction, the samples were warmed to room temperature (which took approximately 15 minutes) and extracted according to the procedure outlined in SW846 Method 8330 (USEPA 1994). Specifically, a 10.0-mL aliquot of acetonitrile (AcN) was added to each sample in a 22-mL scintillation vial. The vials were placed on a vortex mixer for 1 minute and placed in an ultrasonic bath for 18 hours. The temperature of the bath was maintained at less than 25°C with cooling water. The vials were then removed from the bath and allowed to stand undisturbed for 30 minutes. A 2.0-mL aliquot of each extract was removed and combined with 8.0 mL of water. Each solution was then filtered through a Millex SR (0.5-mm) disposable filter, with the first milliliter discarded and the remainder collected in a clean scintillation vial.

RP-HPLC analysis

All samples were analyzed by reversed-phase high performance liquid chromatography (RP-HPLC) on a modular system composed of the following: Spectra-Physics Model SP8800 ternary HPLC pump, a Spectra-Physics Spectra 100 variable wavelength UV detector set at 254 nm (cell path 1 cm), a Dynatech Model LC241 auto sampler equipped with a Rheodyne Model 7125 sample loop injector, and a Hewlett-Packard 3393A digital integrator set to measure peak heights.

All extracts were analyzed on a 15-cm × 3.9-mm LC-8 column (Waters) eluted with 85/15 water/isopropanol (v/v) at 1.4 mL/min. Samples were introduced by overfilling a 100-mL sampling loop. Retention times of the analytes of interest are shown in Table 2. Concentrations were estimated against SARM multianalyte standards.

Table 2. RP-HPLC retention times (minutes) for the analytes of interest.

Analyte	
RDX	3.0
3-NA	3.5
1,3-DNB	4.8
TNT	5.4
2-Am-6-NT	5.9
4-Am-2-NT	6.5
2-Am-4-NT	6.9
2,4-DNT	10.9
2,6-DNT	13.4
4-Am-DNT	15.2
2-Am-DNT	17.2

RESULTS AND DISCUSSION

Concentrations of the spike analytes and transformation products obtained for each soil replicate are presented in Appendix A. Mean concentrations for each time period are presented in Table 3 for the samples stored at all three temperatures.

Results for the time 0 samples at all temperatures demonstrate that, at the start of the incubation, the concentrations of all four of the spike nitroaromatics were near 0.5 mg/kg. The results for the 4-hour samples at 22°C (Table 3a) show that the degradation process at room temperature begins almost immediately and, for some of the analytes, is very rapid. For example, the mean concentration of TNT was reduced from 0.563 mg/kg to 0.461 mg/kg after only 4 hours at 22°C.

Figure 1 shows three chromatograms collected at time 0 and days 1 and 7 for samples stored at room temperature. This figure illustrates several dramatic changes in the sample composition over a relatively short time. First, the height of the peak corresponding to TNT is reduced by half in only 1 day and is only about one-forth its original height in just 7 days. The peak for DNB was also reduced in height substantially over this time, but to a lesser extent than TNT. In contrast, the peaks for 2,4- and 2,6-DNT dropped much less in the first 7 days, indicating that they are more stable in this soil than TNT and DNB.

Evidence that the loss of TNT was partially attributable to a degradation process, and not just poor recovery or irreversible sorption, was the increasing peak height for the two amino reduction products of TNT: 2-Am-DNT and 4-Am-DNT. Likewise, 3-NA, the reduction product of 1,3-DNB, is detectable in the chromatogram as early as the day 1 sample. A plot of the concentration of TNT with time (Fig. 2) shows that the

Table 3. Mean concentration (mg/kg) of analytes in soils incubated at three temperatures.

	RDX	*3-NA*	*DNB*	*TNT*	*2-Am-6NT*	*2-Am-4NT*	*4-Am-2NT*	*2,4-DNT*	*2,6-DNT*	*2-Am-DNT*	*4-Am-DNT*
a. Room temperature (22 ± 2°C).											
0 hr	0.144		0.458	0.563				0.513	0.533		
4 hr	0.141		0.421	0.461				0.472	0.504		
Day 1	0.138	0.020	0.360	0.306				0.428	0.452		0.054
Day 3	0.134	0.040	0.318	0.241				0.433	0.440	0.035	0.084
Day 7	0.138	0.056	0.253	0.173		0.005	0.009	0.396	0.396	0.045	0.095
Day 9	0.137	0.061	0.245	0.165	0.062	0.007	0.010	0.422	0.412	0.049	0.096
Day 13	0.132	0.056	0.187	0.125	0.054	0.010	0.015	0.355	0.323	0.042	0.090
Day 20	0.129	0.046	0.117	0.079	0.048	0.015		0.307	0.239	0.046	0.089
b. 4 ± 1°C.											
0 hr	0.144		0.458	0.563				0.513	0.533		
4 hr	0.141		0.427	0.508				0.466	0.500		
Day 1	0.135		0.414	0.462				0.465	0.485		
Day 3	0.131		0.409	0.448				0.472	0.499		
Day 7	0.138	0.013	0.385	0.387				0.455	0.480	0.020	0.031
Day 13	0.136	0.019	0.348	0.308		0.006	0.007	0.433	0.464	0.020	0.039
Day 20	0.133	0.030	0.307	0.261	0.016	0.014	0.000	0.411	0.430	0.026	0.051
Day 30	0.141	0.058	0.302	0.244	0.029	0.017	0.000	0.457	0.431	0.036	0.067
c. –4 ± 1°C.											
0 hr	0.144		0.458	0.563				0.513	0.533		
4 hr	0.137		0.424	0.513				0.465	0.494		
Day 1	0.145		0.451	0.545				0.506	0.525		
Day 3	0.135		0.422	0.523				0.468	0.498		
Day 7	0.139		0.420	0.522				0.467	0.493		
Day 13	0.130		0.400	0.478				0.451	0.479		
Day 20	0.137		0.403	0.496				0.455	0.482		
Day 30	0.143		0.420	0.498				0.508	0.507		

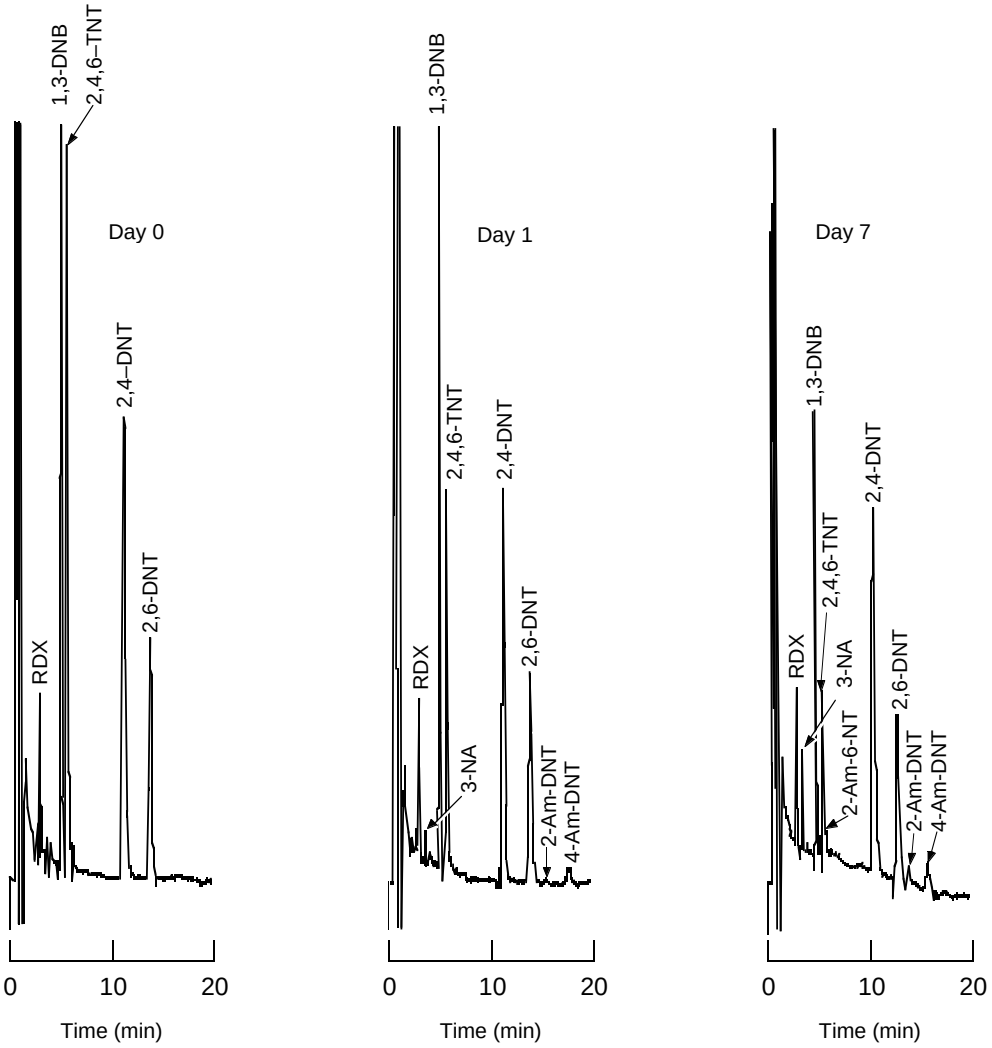


Figure 1. Chromatograms of incubation study samples at room temperature (22 ± 2°C) for Fort Leonard Wood soil.

concentration of TNT drops very rapidly over the first 24 hours, then continues to drop, although less rapidly, thereafter. After 20 days, the concentration of TNT is only one-fifth of the original concentration. The concentration of 2,4-DNT also drops in the first 24 hours, but to a much lesser extent than TNT (Fig. 3). It, too, continues to drop over time, but at the 20-day mark, the concentration of 2,4-DNT is still 60% of the initial value. The two DNTs are also transforming to their corresponding reduction products (2-Am-4NT, 4-Am-2NT, and 2-Am-6NT) as demonstrated by the observation of these three compounds in the room temperature chromatograms after 9 days.

The general pattern seen for the samples stored at 4°C was similar (Table 3b) to that observed for the 22°C samples, except that the rate of reduction was much reduced for all target analytes. Here again, though, the concentrations of TNT and DNB decreased much more rapidly than those of 2,4- and 2,6-DNT. At 4°C, the concentrations of TNT and DNB dropped by 54 and 33%, respectively, in 30 days, while the concentrations of both 2,4- and 2,6-DNT dropped by only 20% in the same time period. The monoamino transformation products of all four nitroaromatics were detectable in the 4°C samples after day 7, again emphasizing that the loss of these compounds was attributable to transformation, not irreversible sorption.

At –4°C, the four key components were shown to be even more stable, with concentrations declining by only about 10% in the 30-day period for all four components (Table 3c).

To investigate the rate of loss and estimate the half-

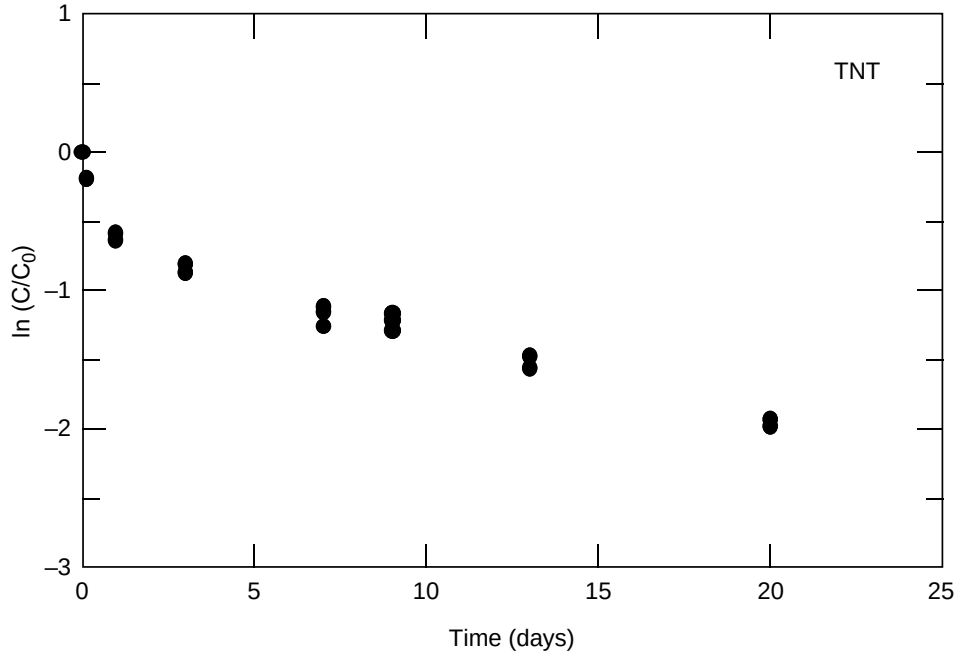


Figure 2. Plot of ln(C/C_0) versus time (days) for TNT at room temperature (22 ± 2°C).

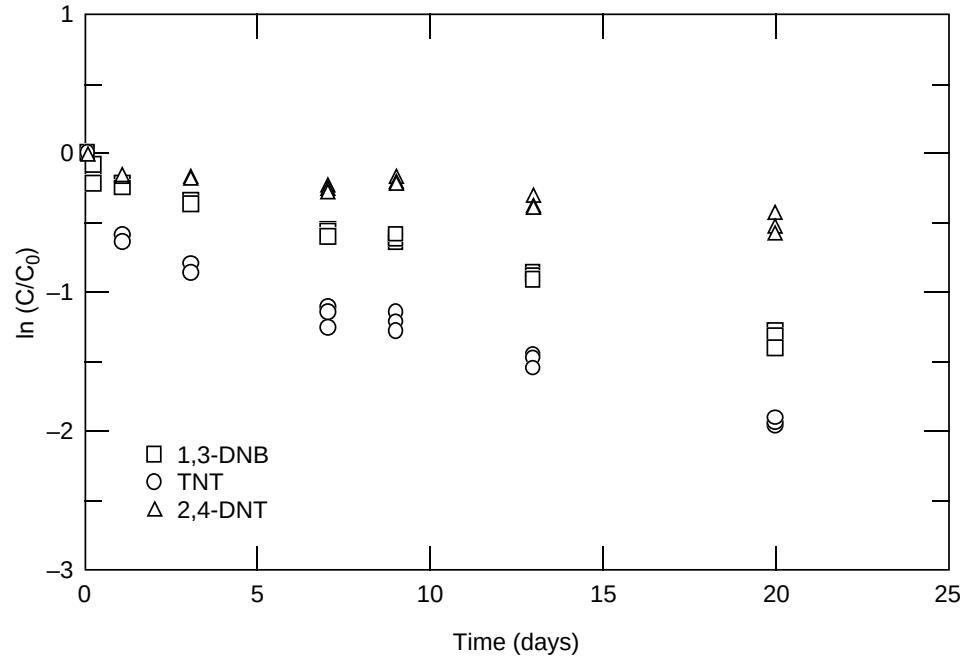


Figure 3. Plot of ln(C/C_0) versus time (days) at room temperature (22 ± 2°C).

lives of these nitroaromatics, the concentrations obtained were plotted as the $\ln(C/C_0)$ versus time (t), where C is the concentration at time t and C_0 is the initial concentration. For a first order rate process, a linear relationship should be obtained. If a process is first order, then the half-life can be determined easily using the simple rate equation:

$$\ln (C/C_0) = kt$$

where k is the rate constant equal to the slope of the curve. The half-life is then calculated by dividing the natural log of 1/2 (–0.693) by the rate constant. An important point to note is that when the rate is first order, the half-life is independent of the starting concentration. Clearly, for the 22°C data, the loss of TNT does not follow simple first order kinetics (Fig. 4). The plot also illustrates that the rate of degradation varies greatly among the different compounds.

The data initially indicate that the rates for the degradation of TNT at room temperature and at 4°C are not first order. Close examination of the data at room temperature reveals that the decay curve for TNT is composed of two linear sections, suggesting sequential first order processes. Although the nature of the two processes is not understood at this time, the data indicate that the first process is very rapid, causing a 50% drop in the concentration of TNT in approximately 1 day. Beyond the first day, the rate of TNT loss is significantly slower. Because the concentration of TNT drops below 50% before the rate of loss slows, the first half-life for TNT at room temperature was estimated using the slope of the data plotted from days 0 through 1. Additional half-lives will be estimated using the slope of the data plotted from days 1 through 30. A similar multi-stage process is indicated for TNT at 4°C, but the first stage is very short, lasting only through the first 4 hours before the slower process takes over. The decrease in TNT concentration during this time is very small, so the half-life here was estimated using the slope of the data plotted beyond the 4-hour mark. Data for TNT at –4°C, as well as for the other three key components at all temperatures, appear to be adequately described by a single first order processes. These data are plotted for 4 and –4°C in Figure 5. Rate equations describing the degradation rates for the primary analytes at all three temperatures were established using the curve fitting functions in SigmaPlot, a commercial plotting package (Table 4). The half-lives for each compound were then estimated by solving each of the functions for time (t) when $\ln (C/C_0)$ is equal to –0.693, that is, one-half of the original concentration (Table 5).

To demonstrate that the rate of degradation also depended on soil type, we compiled the data collected by Grant et al. (1993, 1995) for determining the preextraction holding times for soil samples (Tables A4 to

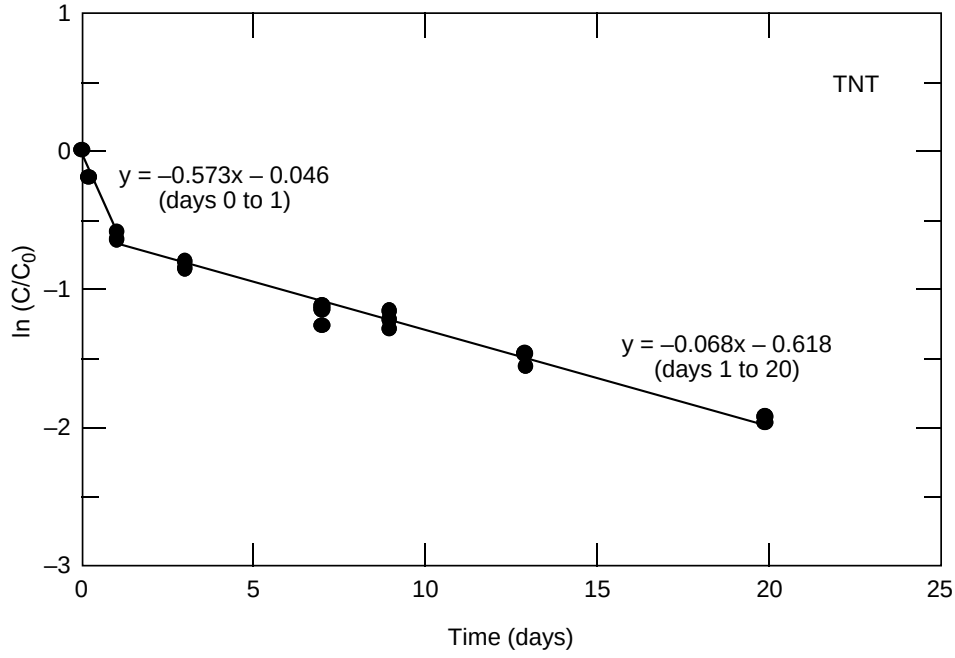
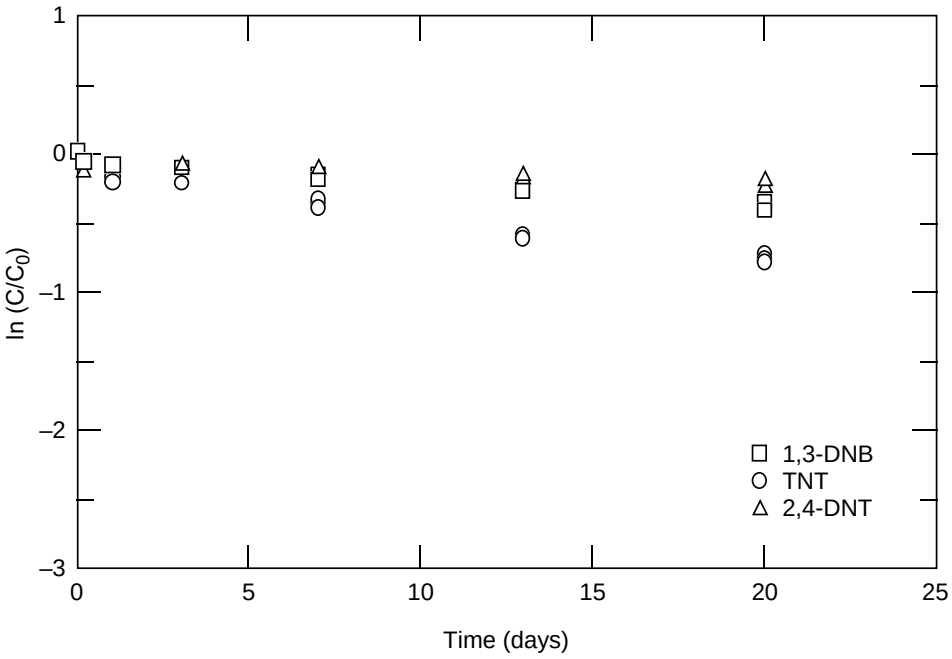
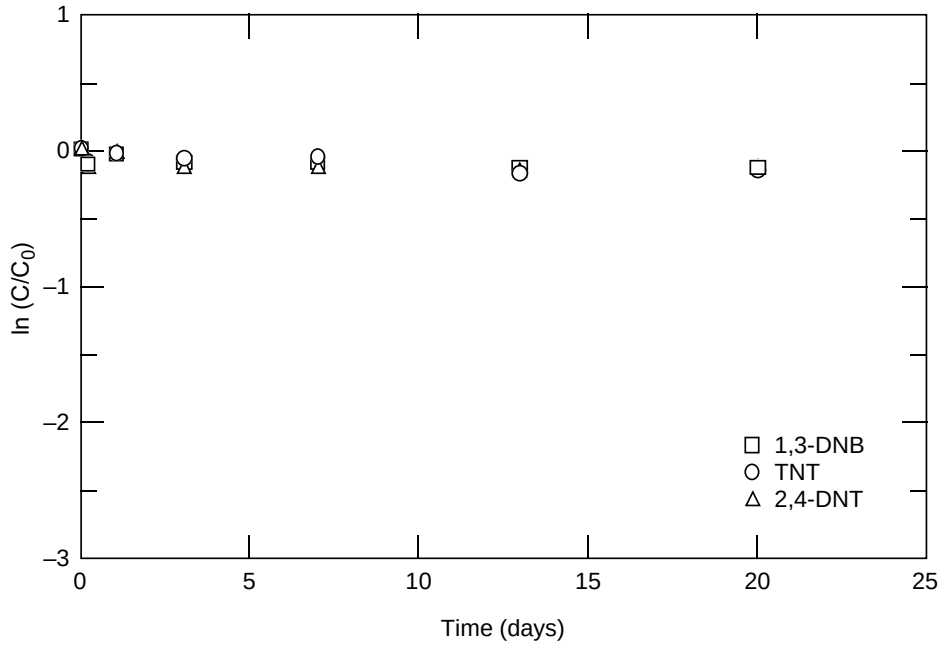


Figure 4. Plot of $\ln(C/C_0)$ versus time (days) for TNT at room temperature (22 ± 2°C) illustrating a multiple stage decay process.



a. 4 ± 1°C.



b. –4 ± 1°C.

Figure 5. Plots of ln(C/C_0) versus time (days) at the two lower temperatures.

Table 4. Rate of loss equations for primary TNT signature analytes in Fort Leonard Wood soil.

Key components	*Temperature (°C)*	*Rate equation**
TNT	22 (0 to 1 days)	$\ln C/C_0 = -0.573t - 0.046$
	22 (1 to 20 days)	$\ln C/C_0 = -0.068t - 0.618$
	4	$\ln C/C_0 = -0.035t - 0.102$
	–4	$\ln C/C_0 = -8.66 \times 10^{-3}t$
1,3-DNB	22	$\ln C/C_0 = -0.070t$
	4	$\ln C/C_0 = -0.021t$
	–4	$\ln C/C_0 = -8.26 \times 10^{-3}t$
2,4-DNT	22	$\ln C/C_0 = -0.027t$
	4	$\ln C/C_0 = -0.013t$
	–4	$\ln C/C_0 = -8.05 \times 10^{-3}t$
2,6-DNT	22	$\ln C/C_0 = -0.039t$
	4	$\ln C/C_0 = -0.011t$
	–4	$\ln C/C_0 = -6.66 \times 10^{-3}t$

**C* is the concentration at time (*t*) and C_0 is the concentration at time zero.

A12). These studies examined the degradation rates of TNT, 2,4-DNT, 1,3,5-trinitrobenzene (TNB), and methyl-2,4,6-trinitrophenylnitramine (tetryl) in three soils, a Windsor silt, a Charlton sandy loam, and a Fort Edwards clay at three temperatures, 22, 4, and –15°C. Data showing the degradation rate of TNT in a deep aquifer soil from the Louisiana Army Ammunition Plant (LAAP) at 22°C were also used (Table A13) (Miyares et al. 1999). Using the same plotting and curve fitting software, we established rate of loss equations for each compound in each soil at each temperature. From the equations, the half-lives were estimated (Table 6).

These data show similar trends with respect to temperature and between analytes as the data for the Fort Leonard Wood soil. The half-lives at lower temperatures are much longer than at room temperature and the half-life of TNT in most cases is significantly shorter than that of 2,4-DNT for each soil type. These data also illustrate the variation in the half-lives of the compounds in the different soils. The half-life of TNT in the Fort Edwards, Windsor, and Charlton soils was less than 1 day, 1.9 days, and 3.5 days, respectively, whereas the half-life for TNT in the LAAP soil was 140 days. This suggests that there are soils in which TNT does not degrade at any appreciable rate. Similar variations are seen for other components as well. Half-lives for all of the analytes in the Fort Edwards soil were shorter by an order of magnitude over the Charlton and Windsor soils, even at the extreme low temperature.

CONCLUSIONS

The nitroaromatic compounds that compose the vapor signature of military grade explosive in land mines have been shown to degrade in soils. Studies investigating the holding times for explosives-contaminated samples have shown rapid to moderate loss of the dif-

Table 5. Half-lives of the primary TNT signature analytes in Fort Leonard Wood soil.

Key components	*Temperature (°C)*	*Half-life (days)*
TNT	22	1.1
	4	17
	–4	80
1,3-DNB	22	9.9
	4	33
	–4	84
2,4-DNT	22	26
	4	53
	–4	86
2,6-DNT	22	18
	4	63
	–4	104

Table 6. Half-lives of explosives determined for a variety of soils.

Soil type	*Key components*	*Temperature (°C)*	*Half-life (days)*
Windsor (silt)	TNB	22	0.49
		2	8.3
		–15	820
	TNT	22	1.9
		2	17
		–15	520
	2,4-DNT	22	50
		2	180
		–15	1100
	tetryl	22	2.2
		2	7.4
		–15	33
Charlton (sandy loam)	TNB	22	1.7
		2	2.9
		–15	480
	TNT	22	3.5
		2	20
		–15	5300
	2,4-DNT	22	53
		2	230
		–15	1100
	tetryl	22	0.39
		2	1.3
		–15	23
Ft. Edwards (clay)	TNB	22	0.62
		2	1.2
		–15	180
	TNT	22	<1
		2	1.4
		–15	170
	2,4-DNT	22	1.5
		2	13
		–15	144
	tetryl	22	0.14
		2	0.21
		–15	26
LAAP (deep aquifer soil)	TNT	22	140

ferent components. These losses varied for each compound and were subject to temperature and soil type. In this study, we investigated the degradation rates of key components of the chemical vapor signatures from the explosive charge in land mines. We estimated the half-lives for these chemical components in soil from a research minefield at Fort Leonard Wood, Missouri, at several different temperatures. Half-lives at room temperature ranged from 1.4 days for TNT to 26 days for 2,4-DNT. Samples stored at lower temperatures showed longer half-lives. Degradation rates were also found to vary with soil type. The half-life of TNT at room temperature in Fort Edwards clay was determined to be less than 1 day, in Windsor and Charlton soils it was 1.9 and 1.7 days, respectively, and in deep aquifer soil from LAAP, 140 days.

Our results demonstrated that the rate of degradation of the principal chemical components in the vapor signature vary significantly. TNT, DNB, and TNB have half-lives that are significantly shorter than those of 2,4-DNT and 2,6-DNT. The results also demonstrate that these rates are subject to the effects of temperature and soil type.

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APPENDIX A: DATA

Table A1. Concentration (mg/kg) of analytes in soil incubated at room temperature (22 ± 2°C).

Incubation period	*RDX*	*3-NA*	*DNB*	*TNT*	*2-Am-6NT*	*2-Am-4NT*	*4-Am-2NT*	*2,4-DNT*	*2,6-DNT*	*2-Am-DNT*	*4-Am-DNT*
0 hr	0.148	0.462	0.566				0.524	0.530			
0 hr	0.142		0.451	0.559				0.503	0.529		
0 hr	0.143		0.461	0.563				0.513	0.539		
4 hr	0.146		0.418	0.466				0.468	0.497		
4 hr	0.138		0.425	0.453				0.478	0.509		
4 hr	0.138		0.419	0.464				0.471	0.507		
Day 1	0.140	0.021	0.356	0.294				0.426	0.458		0.056
Day 1	0.138	0.021	0.358	0.314				0.428	0.456		0.052
Day 1	0.135	0.017	0.368	0.310				0.432	0.443		0.055
Day 3	0.132	0.041	0.315	0.237				0.430	0.448	0.035	0.083
Day 3	0.133	0.040	0.318	0.235				0.434	0.426	0.034	0.085
Day 3	0.137	0.038	0.322	0.253				0.436	0.446	0.035	0.085
Day 7	0.138	0.055	0.257	0.184		0.005	0.009	0.403	0.403	0.045	0.102
Day 7	0.136	0.057	0.254	0.176		0.007	0.009	0.398	0.395	0.041	0.089
Day 7	0.140	0.055	0.247	0.159		0.004	0.009	0.386	0.391	0.048	0.093
Day 9	0.137	0.062	0.237	0.164		0.007	0.009	0.415	0.407	0.048	0.099
Day 9	0.141	0.061	0.253	0.177	0.062	0.008	0.011	0.431	0.420	0.051	0.096
Day 9	0.133	0.058	0.246	0.153		0.006	0.010	0.419	0.409	0.047	0.093
Day 13	0.134	0.057	0.191	0.130		0.013	0.020	0.373	0.345	0.042	0.088
Day 13	0.134	0.056	0.188	0.127	0.056	0.011	0.015	0.351	0.306	0.039	0.093
Day 13	0.128	0.054	0.181	0.118	0.051	0.007	0.010	0.342	0.320	0.046	0.089
Day 13*	0.125	0.059	0.198	0.132		0.008	0.012	0.373	0.332	0.043	0.093
Day 13*	0.139	0.059	0.199	0.136	0.061	0.010	0.014	0.370	0.353	0.047	0.092
Day 13*	0.138	0.057	0.192	0.125		0.010	0.011	0.364	0.344	0.042	0.097
Day 20	0.140	0.049	0.123	0.082	0.054	0.020	0.000	0.331	0.256	0.059	0.102
Day 20	0.130	0.047	0.120	0.079	0.046	0.016	0.000	0.304	0.238	0.038	0.084
Day 20	0.118	0.042	0.109	0.077	0.043	0.009	0.000	0.285	0.225	0.041	0.083

*Day 13 sample extracts were analyzed in duplicate for quality control (qc) purposes.

Table A2. Concentration (mg/kg) of analytes in soil incubated at 4 ± 1°C.

Incubation period	*RDX*	*3-NA*	*DNB*	*TNT*	*2-Am-6NT*	*2-Am-4NT*	*4-Am-2NT*	*2,4-DNT*	*2,6-DNT*	*2-Am-DNT*	*4-Am-DNT*
0 hr	0.148		0.462	0.566				0.524	0.530		
0 hr	0.142		0.451	0.559				0.503	0.529		
0 hr	0.143		0.461	0.563				0.513	0.539		
4 hr	0.147		0.426	0.505				0.451	0.498		
4 hr	0.138		0.429	0.512				0.473	0.502		
4 hr	0.139		0.425	0.506				0.474	0.501		
Day 1	0.141		0.424	0.473				0.476	0.487		
Day 1	0.136		0.407	0.455				0.461	0.488		
Day 1	0.127		0.409	0.457				0.458	0.481		
Day 3	0.120		0.409	0.447				0.470	0.495		
Day 3	0.138		0.408	0.449				0.470	0.500		
Day 3	0.135		0.410	0.448				0.475	0.503		
Day 7	0.130	0.014	0.375	0.375				0.444	0.460	0.025	0.029
Day 7	0.140	0.014	0.390	0.397				0.457	0.490	0.015	0.035
Day 7	0.143	0.013	0.389	0.390				0.463	0.491	0.019	0.028
Day 13	0.131	0.017	0.346	0.312		0.004	0.009	0.428	0.457	0.021	0.033
Day 13	0.136	0.018	0.349	0.312		0.009		0.436	0.469	0.024	0.040
Day 13	0.140	0.020	0.349	0.300		0.004	0.005	0.434	0.465	0.016	0.045
Day 13*	0.133	0.018	0.354	0.324		0.006		0.438	0.470	0.023	0.032
Day 13*	0.134	0.020	0.353	0.307		0.005	0.008	0.444	0.464	0.022	0.047
Day 13*	0.138	0.022	0.353	0.312		0.009	0.016	0.442	0.476	0.028	0.047
Day 20	0.130	0.030	0.298	0.254	0.024	0.016	0.000	0.405	0.428	0.026	0.055
Day 20	0.135	0.032	0.318	0.272	0.025	0.015	0.000	0.425	0.433	0.026	0.048
Day 20	0.136	0.029	0.306	0.258	0.000	0.010	0.000	0.405	0.430	0.027	0.051
Day 30	0.137	0.096	0.295	0.241	0.025	0.013	0.000	0.447	0.429	0.041	0.065
Day 30	0.144	0.042	0.304	0.242	0.030	0.019	0.000	0.466	0.433	0.031	0.058
Day 30		0.036	0.306	0.249	0.031	0.020	0.000	0.457	0.432	0.036	0.076

*Day 13 sample extracts were analyzed in duplicate for quality control (qc) purposes.

Table A3. Concentration (mg/kg) of analytes in soil incubated at –4 ± 1°C.

Incubation period	*RDX*	*3-NA*	*DNB*	*TNT*	*2-Am-6NT*	*2-Am-4NT*	*4-Am-2NT*	*2,4-DNT*	*2,6-DNT*	*2-Am-DNT*	*4-Am-DNT*
0 hr	0.148		0.462	0.566				0.524	0.530		
0 hr	0.142		0.451	0.559				0.503	0.529		
0 hr	0.143		0.461	0.563				0.513	0.539		
4 hr	0.137		0.426	0.516				0.471	0.498		
4 hr	0.141		0.429	0.514				0.457	0.499		
4 hr	0.134		0.418	0.508				0.466	0.486		
Day 1	0.148		0.451	0.547				0.512	0.521		
Day 1	0.142		0.446	0.540				0.502	0.526		
Day 1	0.147		0.456	0.548				0.503	0.529		
Day 3	0.134		0.424	0.526				0.468	0.498		
Day 3	0.138		0.425	0.530				0.474	0.501		
Day 3	0.132		0.418	0.514				0.463	0.495		
Day 7	0.136		0.423	0.526				0.476	0.499		
Day 7	0.146		0.427	0.530				0.476	0.497		
Day 7	0.137		0.410	0.509				0.450	0.485		
Day 13	0.134		0.400	0.476				0.449	0.472		
Day 13	0.129		0.393	0.472				0.443	0.476		
Day 13	0.128		0.406	0.487				0.460	0.488		
Day 13*	0.137		0.399	0.475				0.454	0.480		
Day 13*	0.136		0.396	0.471				0.446	0.475		
Day 13*	0.135		0.403	0.484				0.452	0.482		
Day 20	0.133		0.392	0.486				0.445	0.467		
Day 20	0.139		0.409	0.504				0.458	0.492		
Day 20	0.139		0.408	0.499				0.463	0.486		
Day 30	0.142		0.409	0.486				0.491	0.493		
Day 30	0.145		0.434	0.510				0.522	0.520		
Day 30	0.142		0.418	0.497				0.511	0.506		

*Day 13 sample extracts were analyzed in duplicate for quality control (qc) purposes.

Table A4. Concentration (mg/kg) of analytes in Windsor soil incubated at room temperature (22 ± 2°C).

Time (days)	*TNB*	*TNT*	*2,4-DNT*	*Tetryl*
0	0.914	0.969	0.850	5.48
1				3.16
3	0.013	0.465	0.741	1.63
7		0.067	0.716	0.66
14			0.626	
28			0.573	
56			0.419	

Table A5. Concentration (mg/kg) of analytes in Windsor soil incubated at 4 ± 1°C.

Time (days)	*TNB*	*TNT*	*2,4-DNT*	*Tetryl*
0	0.914	0.969	0.850	5.48
1				3.92
3	0.598	0.861	0.802	4.15
7	0.300	0.777	0.837	2.94
14	0.090	0.637	0.828	
28		0.309	0.772	
56	0.013	0.086	0.675	

Table A6. Concentration (mg/kg) of analytes in Windsor soil incubated at −15 ± 2°C.

Time (days)	*TNB*	*TNT*	*2,4-DNT*	*Tetryl*
0	0.914	0.969	0.850	5.48
1				5.00
3	0.885	0.926	0.799	4.44
7	0.946	0.975	0.863	5.10
14	0.952	0.978	0.856	
28	0.937	0.980	0.857	
56	0.949	0.954	0.808	

Table A7. Concentration (mg/kg) of analytes in Charlton soil incubated at room temperature (22 ± 2°C).

Time (days)	*TNB*	*TNT*	*2,4-DNT*	*Tetryl*
0	0.817	0.977	0.860	5.58
1				0.30
3	0.119	0.437	0.793	0.04
7	0.059	0.190	0.751	0.04
14		0.072	0.667	
28			0.574	
56		0.008	0.426	

Table A8. Concentration (mg/kg) of analytes in Charlton soil incubated at 2 ± 1°C.

Time (days)	*TNB*	*TNT*	*2,4-DNT*	*Tetryl*
0	0.817	0.977	0.860	5.58
1				2.82
3	0.320	0.876	0.828	0.91
7	0.108	0.702	0.783	0.17
14	0.054	0.601	0.843	
28		0.372	0.803	
56	0.013	0.225	0.726	

Table A9. Concentration (mg/kg) of analytes in Charlton soil incubated at −15 ± 2°C.

Time (days)	*TNB*	*TNT*	*2,4-DNT*	*Tetryl*
0	0.817	0.977	0.860	5.58
1				4.07
3	0.820	0.940	0.813	4.47
7	0.854	0.963	0.850	5.00
14	0.884	0.993	0.869	
28	0.833	0.944	0.825	
56	0.879	0.984	0.839	

Table A10. Concentration (mg/kg) of analytes in Fort Edwards clay incubated at room temperature (22 ± 2°C).

Time (days)	*TNB*	*TNT*	*2,4-DNT*	*Tetryl*
0	0.566	0.596	0.875	4.43
1				0.03
3	0.020		0.226	
7			0.194	
14			0.113	
28			0.060	
56			0.047	

Table A11. Concentration (mg/kg) of analytes in Fort Edwards clay incubated at 2 ± 1°C.

Time (days)	*TNB*	*TNT*	*2,4-DNT*	*Tetryl*
0	0.566	0.596	0.875	4.43
1				0.17
3	0.102	0.130	0.768	0.06
7			0.586	0.04
14			0.426	
28			0.391	
56			0.315	

Table A12. Concentration (mg/kg) of analytes in Fort Edwards clay incubated at –15 ± 2°C.

Time (days)	*TNB*	*TNT*	*2,4-DNT*	*Tetryl*
0	0.566	0.596	0.875	4.43
1				3.75
3	0.609	0.530	0.840	3.43
7	0.477	0.479	0.719	4.05
14	0.538	0.553	0.783	
28	0.480	0.504	0.749	
56	0.477	0.500	0.697	

Table A13. Concentration (mg/kg) of analytes in LAAP soil incubated at room temperature (22 ± 2°C).

Time (days)	*TNT*	*2-Am-DNT*	*4-Am-DNT*
0	6.21	0.018	
1	6.02	0.023	
3	6.14	0.021	
7	5.90	0.014	
14	6.18	0.042	0.096
28	4.71	0.071	0.167
77	4.35	0.137	0.290

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
September 2000	Technical Report	

4. TITLE AND SUBTITLE

Estimating the Half-Lives of Key Components of the Chemical Vapor Signature of Land Mines

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Paul H. Miyares and Thomas F. Jenkins

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

U.S. Army Engineer Research and Development Center
Cold Regions Research and Engineering Laboratory
72 Lyme Road
Hanover, New Hampshire 03755-1290

8. PERFORMING ORGANIZATION REPORT NUMBER

ERDC/CRREL TR-00-17

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Defense Advanced Research Projects Agency (DARPA)
3701 Fairfax Drive
Arlington, VA 22203

10. SPONSOR / MONITOR'S ACRONYM(S)

11. SPONSOR / MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

Available from NTIS, Springfield, Virginia 22161.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

The qualitative composition of the chemical signature of TNT-filled land mines is predominantly the isomers of dinitrotoluene (DNT), dinitrobenzene (DNB), and trinitrotoluene (TNT). These chemicals are known to undergo transformation in the soil under aerobic conditions, creating corresponding chemicals in which one of the nitro groups has been converted to an amino function. For these signatures to be available at the ground surface for detecting buried mines, the stability of these chemicals in the soil must exceed their rate of transport through the soil to the surface. This research investigates the rate of transformation of the major components of the signature of TNT-filled land mines in soil. A series of 5.0-g replicate portions of soil from a research minefield at Fort Leonard Wood, Missouri, was fortified with 2,4,6-trinitrotoluene, 2,4- and 2,6-dinitrotoluene, and 1,3-dinitrobenzene at about 0.5 mg/kg. Replicates were held at one of three temperatures (22 ± 2, 4 ± 2, or -4 ± 2°C) in the dark for periods ranging from 4 hours to 30 days and were then extracted with acetonitrile. The extracts were analyzed by reversed-phase HPLC to estimate the concentrations of the parent compounds and any detectable transformation products remaining. Concentrations of these compounds were plotted versus time and the rate of transformation for each compound estimated. While it doesn't appear that the process is kinetically first order, the half-life at 22°C was estimated to be about 1.3 days for 2,4,6-TNT, 9.9 days for 1,3-DNB, 18 days for 2,6-DNT, and 26 days for 2,4-DNT. At lower temperatures the half-lives were considerably longer, as expected.

15. SUBJECT TERMS

2,4-DNT
Chemical signatures
Explosives
Half-lives
Land mine detection
TNT

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER *(include area code)*
U	U	U	U	25	